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13. ABSTRACT (Maximum 200 words)

The lifetime of thermally fixed photorefractive holograms in iron doped lithium niobate was investigated. A prescription for material preparation and fixing technique was developed that enables a thermally fixed hologram to be recorded in Fe-doped $LiNbO_3$ with high diffraction efficiency and long lifetime. In particular, a hologram with a fixed photorefractive index modulation of ~10^{-3} and a 100 year lifetime at room temperature is predicted. A lithium niobate crystal was processed according to the prescription and a thermally fixed hologram was recorded at high temperature. The projected lifetime of the hologram at 25 °C was shown to be ~110 years.

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DEVELOPMENT OF LONG LIFETIME PHOTOREFRACTIVE
CRYSTALS FOR HOLOGRAPHIC DATA STORAGE

FINAL PROGRESS REPORT

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April 30, 1998

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Holographic data storage in photorefractive crystals is a subject of considerable current and commercial interest.[1-3] It is driven by the prospects of large storage capacity memories with V/λ^3 bits in a volume V. Two of the important concerns in this field involve the lifetime of fixed holograms and their diffraction efficiency. Volume phase holograms in photorefractive materials are produced by the redistribution of photoexcited charge carriers in the presence of light. To avoid fast optical erasure of the holograms during readout several techniques have been developed.[4-7] In general, efficient ionic fixing is based on the great disparity between the dark electronic conductivity at elevated temperatures and the ionic conductivity. At moderately high temperatures the ionic conductivity is dominant, and ions readily compensate for the holographic electric field pattern created by photoexcited electrons by mimicking their spatial distribution. At low temperatures the ionic conductivity is also low, permitting the quasi-permanent storage of the ionic replica of the initial electronic hologram. The residual ionic conductivity at low temperature thus determines the lifetime of the fixed hologram.
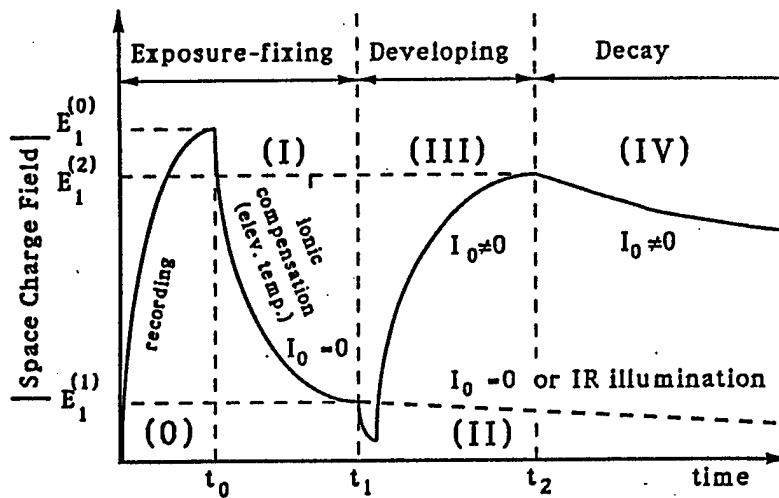

Figure 1: A typical life history of a hologram in a photorefractive material.

A typical history of a fixed hologram recorded using the sequential fixing technique (to be described later) is sketched in Figure 1. In phase I an electronic grating, previously exposed, is heated to cause ionic transport. This leads to a compensated grating, which is represented by the net space charge field amplitude $E_1^{(1)}$. In phase II the

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grating is left in the dark or is exposed to infrared light, which is not photoactive. This stage corresponds to a slow dark decay of both the electronic grating and the ionic compensating grating, which adiabatically follows the former. In holographic data storage as well as many other applications, however, the hologram is exposed to a reading light as in phase III. This light causes a partial redistribution of the trapped electrons, culminating in a quasi-stable field $E_1^{(2)}$. This field will then proceed to decay to zero under illumination in phase IV because of ionic transport.

The problem of grating dynamics in photorefractive crystals has been considered extensively,[8-14] especially in iron doped lithium niobate. Fe-doped $LiNbO_3$ has been, and probably still is, one of the most promising volume holographic recording materials due to an efficient thermal fixing mechanism,[4] its commercial availability in large sizes,[15] and the fact that it has been the subject of study for over thirty years.[16] Two extreme cases of fixed photorefractive behavior have been identified in Fe-doped $LiNbO_3$, producing either long lifetime, but low diffraction efficiency, compensated holograms or high diffraction efficiency, but short lifetime, developed holograms. A basic difference between the two is the degree of space charge field compensation by mobile charges. If the compensation is large, only a fraction of the photorefractive space charge distribution is revealed, and the resulting diffraction efficiency is reduced. However, the lifetime of the hologram is increased since its decay is slowed down by the charge screening. This trade-off is reciprocal and is determined by the development efficiency γ, which is given by

$$\gamma := \frac{\left(E_0 + E_{pv}\cdot x\right) + i\cdot E_d}{\left(E_0 + E_{pv}\cdot x\right) + i\cdot\left(E_q + E_d\right)}, \qquad (1)$$

where E_0 is the DC electric field, $E_d \equiv k_B T K/e$ is the diffusion field, and $E_{pv} \equiv J_{pv}/\sigma_p = \kappa\alpha I/\sigma_p$ is the photovoltaic field with κ, α, I, and σ_p equal to the photovoltaic constant, absorption coefficient, light intensity, and photoconductivity, respectively. Assuming that Fe is present in only two valence states, Fe^{2+} and Fe^{3+}, and negligible hole transport, then $E_q \equiv ex(1-x)[Fe]/\epsilon K$ is the limiting space charge field, where $x \equiv [Fe^{3+}]/[Fe]$ is the oxidation state, $[Fe] = [Fe^{2+}] + [Fe^{3+}]$, and $[\cdot]$ denotes concentration. In general, $0 \leq x \leq 1$ and a completely oxidized crystal is characterized by $x = 1$. Also, $|\gamma| \leq 1$. When $|\gamma| = 1$,

no charge compensation or screening takes place and any immobile space charge modulation is completely revealed.

Given a fixed ionic space charge modulation ΔN_i, the developed space charge field can be written as

$$\Delta E = ie(\Delta N_i)\gamma/\varepsilon K . \qquad (2)$$

Obviously, a large γ is desirable for maximum diffraction efficiency. This field will decay in a damped, oscillatory manner with a complex time constant

$$\tau = (\omega_i\gamma + D_iK^2)^{-1} \approx (\omega_i\gamma)^{-1} , \qquad (3)$$

since, typically, $\omega_i\gamma \gg D_iK^2$ in Fe-doped LiNbO$_3$, where ω_i and D_i are the ionic relaxation rate and diffusion constant, respectively. An approximate, but conservative measure of the effective lifetime of the developed hologram can be defined as

$$\tau_{eff} = M\omega_i^{-1} , \qquad (4)$$

where $M \equiv |\gamma|^{-1}$ is the lifetime multiplier. For long hologram lifetimes, small values of ω_i and γ are required, which in general reduce the strength of the developed hologram.

The largest thermally fixed space charge fields are obtained[17,18] in heavily iron doped lithium niobate samples grown from melts containing as much as 0.15 mole % Fe$_2$O$_3$. At these dopant densities, the photorefractive effect is dominated by the photovoltaic current. Therefore, the c-axes of these crystals need to be electrically short-circuited, otherwise large DC photovoltaic fields will form during illumination and substantially limit the resulting photorefractive index changes. With $E_0 = 0$, $|\gamma|$ and M are plotted in Figures 2 and 3 as a function of the oxidation state x, which is the only free material parameter remaining. Using the sequential fixing technique whereby holograms are written at room temperature, fixed in the dark at an elevated temperature, and then developed at room temperature, Figures 4 and 5 show the fixed ionic space charge modulation ΔN_i and the corresponding developed space charge field ΔE from Equation (2). ΔN_i is given by

$$\Delta N_i := -m \cdot \left(\frac{\varepsilon \cdot K}{e} \right) \cdot E_q \cdot \frac{E_{pv} + i \cdot E_d}{E_{pv} \cdot x + i \cdot (E_q + E_d)} , \qquad (5)$$

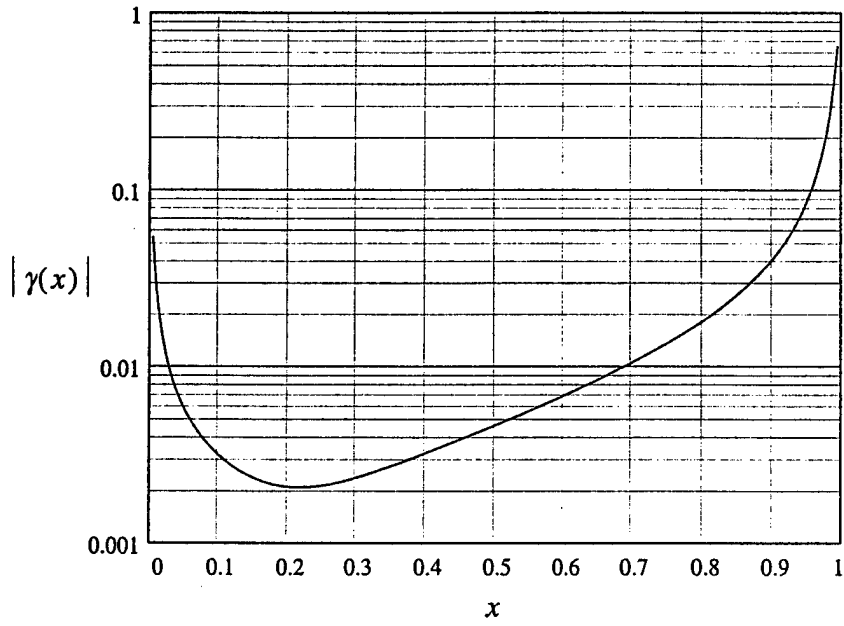where m is the modulation index of the interference pattern. This result is based on the

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Figure 2: Development efficiency versus oxidation state of an Fe-doped $LiNbO_3$ crystal with $[Fe] = 2.5 \cdot 10^{19} cm^{-3}$, $E_{pv} = 2 \cdot 10^{-15} \cdot [Fe^{3+}] V/cm$, $E_0 = 0, 2\pi/K = 0.5\mu m$, and $\varepsilon = 32\varepsilon_0$.
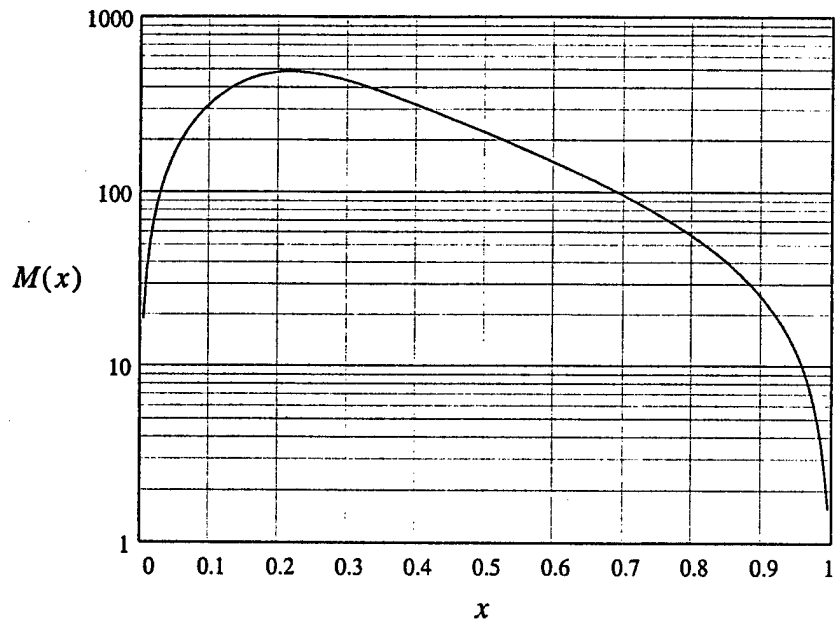

Figure 3: Lifetime multiplier versus oxidation state for the crystal described in Figure 2.

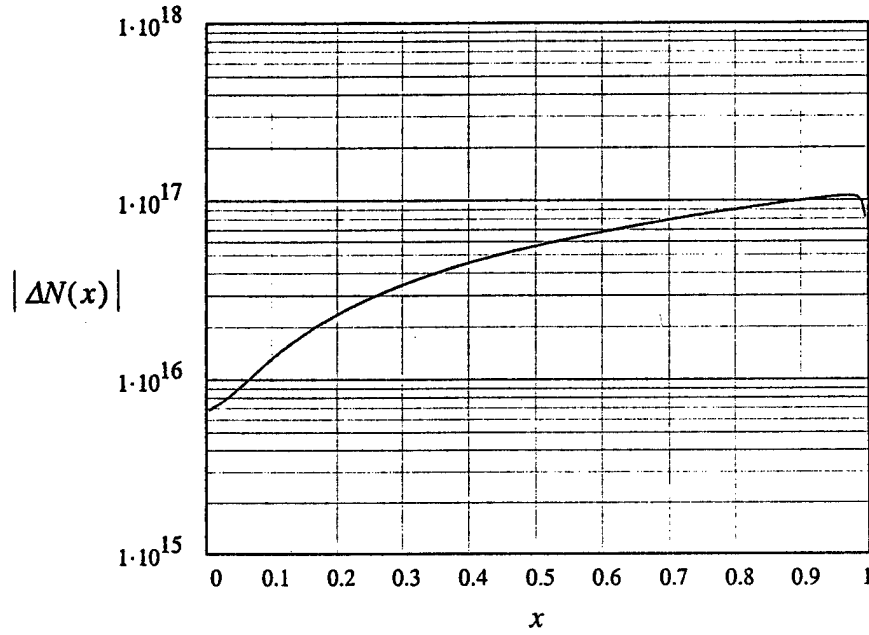Figure 4:   Fixed ionic space charge modulation (cm^{-3}) versus
             oxidation state of a saturated hologram recorded in
             the crystal described in Figure 2 using the sequential
             fixing technique with m=1.

assumption that the LiNbO$_3$ crystal contains a sufficiently large number of mobile ions to completely compensate the photorefractive space charge field during the fixing step, which is invariably the case if the fixing temperature is high enough.

From Figure 5 it is apparent that the crystal should be fully oxidized to maximize the developed space charge field. However, the lifetime multiplier M (see Figure 3) decreases rapidly with increasing x, thus limiting the effective lifetime of the fixed hologram. Because of this trade-off, ω_i^{-1} must be increased substantially from its typical, as-grown value of a few months at room temperature to get high diffraction efficiency holograms with reasonably long lifetimes of, say, >10 years.

To do so, the transport properties of the fixing ions need to be understood and controlled. It has been shown that protons are the mobile fixing ions in as-grown LiNbO$_3$.[19] By measuring the optical absorption at 2.87 μm with an infrared spectrometer, a crystal's OH$^-$ concentration, denoted by [OH$^-$], and proton density can be determined.

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As-grown $LiNbO_3$ is characterized by a large [OH⁻]. Since the ionic relaxation time ω_i^{-1} is inversely proportional to the proton concentration, by reducing the [OH⁻] of the crystal the lifetime of a fixed hologram can be increased.
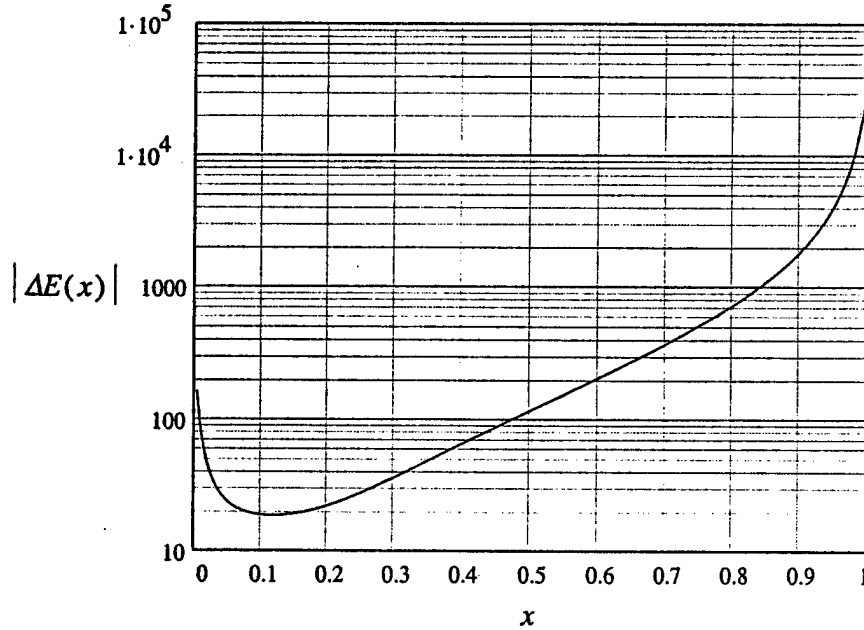

Figure 5:   Developed space charge field (v/cm) versus oxidation state
              of a saturated hologram recorded in the crystal described
              in Figure 2 using the sequential fixing technique with m = 1.

Ionic relaxation times were measured with the experimental arrangement shown in Figure 6. At a constant, elevated temperature a photorefractive grating is written in a Fe-doped $LiNbO_3$ crystal with an argon ion laser. After the writing beams are turned off, the decay of the hologram is monitored by a weak, Bragg matched He-Ne probe beam. A typical response is given in Figure 7 in which both phase I (ionic) and phase II (compensated electronic) decay are apparent (see Figure 1). Once the data are recorded, the temperature is changed, and the experiment is repeated. By fitting an exponential to the Phase I portions of the curves, ω_i^{-1} as a function of temperature can be determined. In this manner the thermal activation energies of the fixing ions in the $LiNbO_3$ crystals can be obtained and used to extrapolate holographic lifetimes to room temperature. Actual data for an as-grown sample and one that was processed to reduce its [OH⁻] are shown in Figure 8.
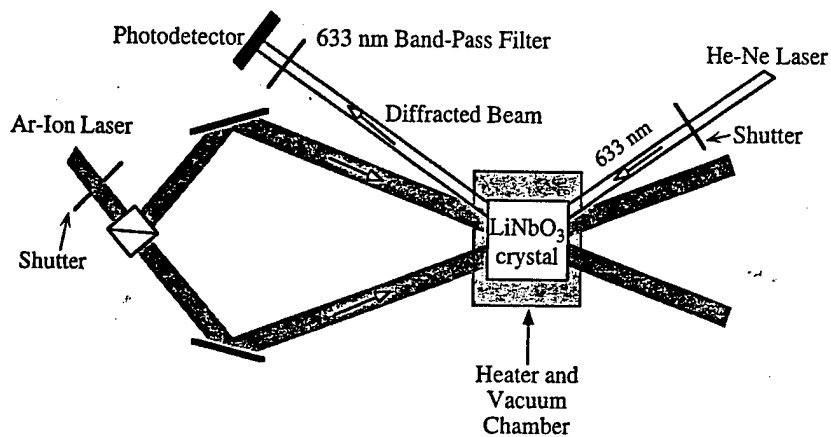
Figure 6:   Experimental arragement used to measure hologram lifetimes.
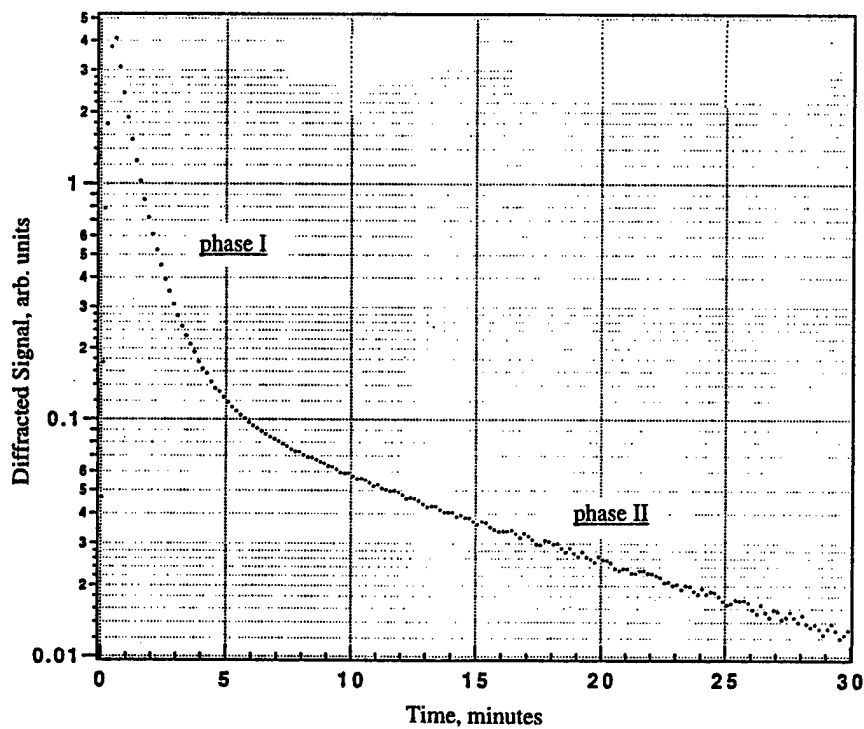

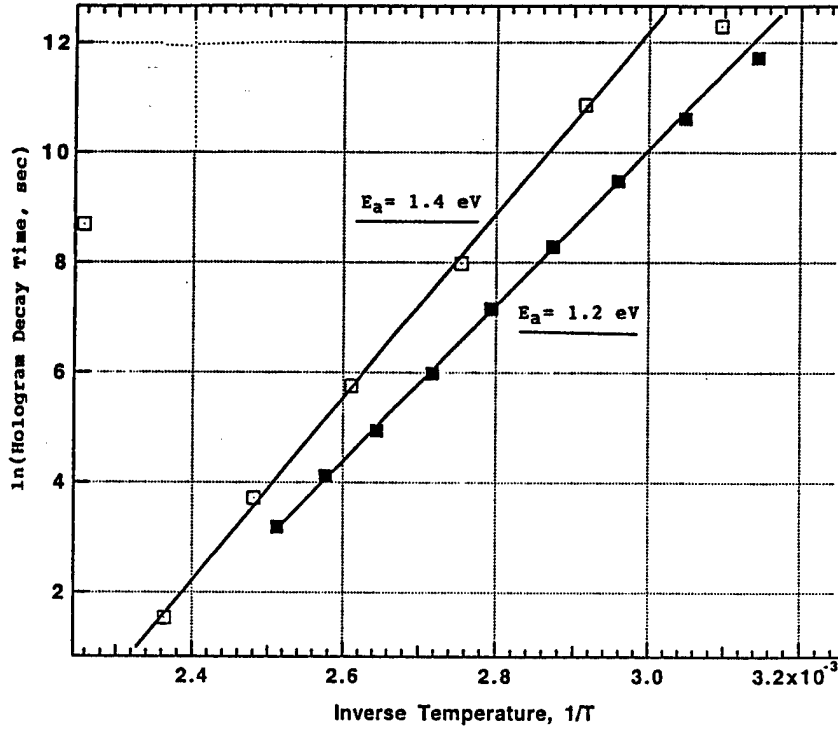Figure 7:   Typical hologram decay behavior at 130°C.

Figure 8: Hologram decay times versus temperature.

We find in as-grown lithium niobate crystals with typically high proton concentration that the ionic relaxation time exhibits a 1.2 eV thermal activation energy at elevated temperatures, which is characteristic of protonic conductivity.[20] At room temperature ω_i^{-1} is about 70 days. A significant increase in ω_i^{-1} can be achieved by substantially reducing the OH^- concentration in the as-grown samples. This dehydration is accomplished by a post-growth, high temperature annealing process using a water and hydrocarbon free O_2 gas flow.

This high temperature treatment can decrease the concentration of protons in a $LiNbO_3$ crystal by a factor of ~100. For the processed sample referred to in Figure 8, the optical absorption coefficient α_{OH} at 2.87 µm due to OH^- ions was reduced from a typical, as-grown value of 0.7 cm^{-1} to <0.01 cm^{-1}, indicating a >70 times decrease in proton density. As expected, the ionic relaxation time in the dehydrated crystals increased substantially. Quite unexpectedly, though, the thermal activation energy of ω_i^{-1} at

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elevated temperatures increased to 1.4 eV. Moreover, ω_i^{-1} did not depend on proton concentration anymore.

These results suggest that the mobile fixing ions in dehydrated crystals are not protons, but some more thermally stable species. Since the $LiNbO_3$ crystals used in this research were of the congruent composition, lithium vacancies were immediately suspected. A holographic lifetime experiment was performed on a sample whose composition was forced closer to stoichiometry using the vapor transport equilibration technique.[21,22] Although there were significantly fewer Li vacancies in the crystal now, the holographic lifetimes did not change appreciably. Therefore, it is unlikely that Li vacancies are involved in the fixing process, and the identity of the 1.4 eV species remains unknown.

From the high temperature data, nonetheless, ionic relaxation times of ~2 years at room temperature are projected for the samples with the 1.4 eV activation energy. These results represent an order of magnitude increase in ω_i^{-1} over the nominal 2 - 3 months that is obtained with the as-grown crystals. To increase the lifetime beyond 2 years, however, the identity of the 1.4 eV species will need to be determined so that their concentration can be controlled and reduced.

Although dehydration of Fe-doped $LiNbO_3$ can be used to increase the ionic relaxation time,[23] dehydrated crystals cannot be completely oxidized even in pure O_2, if the gas has been dried and removed of hydrocarbons to reduce the OH^- concentration in the samples. In fact, such an atmosphere is slightly reducing and typically yields an oxidation state $x < 0.9$. This is because oxygen probably does not enter or leave $LiNbO_3$ by itself, but rather as Li_2O or H_2O,[24] so that some water vapor is needed to facilitate oxidation. Thus, the use of the sequential fixing technique with dehydrated crystals remains limited by the trade-off between high diffraction efficiency and long hologram lifetime.

It is known that the simultaneous fixing method yields holograms with larger diffraction efficiencies than the sequential approach.[25] Here the recording is performed at high temperature where the fixing ions are mobile enough to compensate the photorefractive space charge field in real-time. Afterward, the crystal is cooled and the

hologram is developed at room temperature as before. Since the recording and readout temperatures are different, the change in the Bragg condition of the hologram must also be considered. For wavelength multiplexed holograms,[26] a small shift in the readout wavelength (~0.5 nm) is usually sufficient to restore the Bragg condition. Using the same assumptions as before, the fixed ionic space charge modulation for the simultaneous fixing method is given by

$$\Delta N_i := -i \cdot m \cdot \left(\frac{\varepsilon \cdot K}{e} \right) \cdot E_q \cdot \frac{E_{pv} + i \cdot E_d}{E_{pv} \cdot x + i \cdot E_d}, \qquad (6)$$

and is plotted in Figure 9. The developed space charge field ΔE follows directly from Equation (2) and is shown in Figure 10.
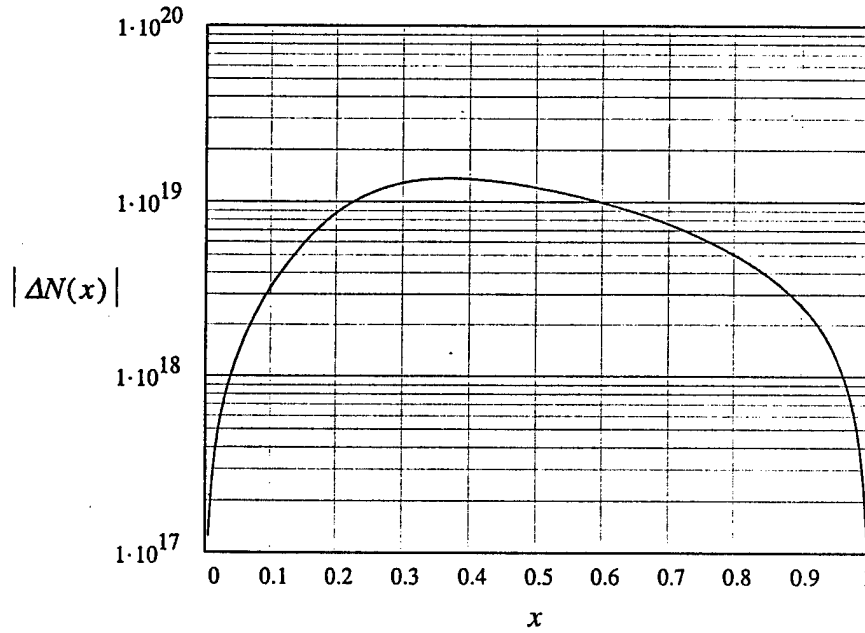

Figure 9: Fixed ionic space charge modulation (cm^{-3}) versus oxidation state of a saturated hologram recorded in the crystal described in Figure 2 using the simultaneous fixing technique with m=1.
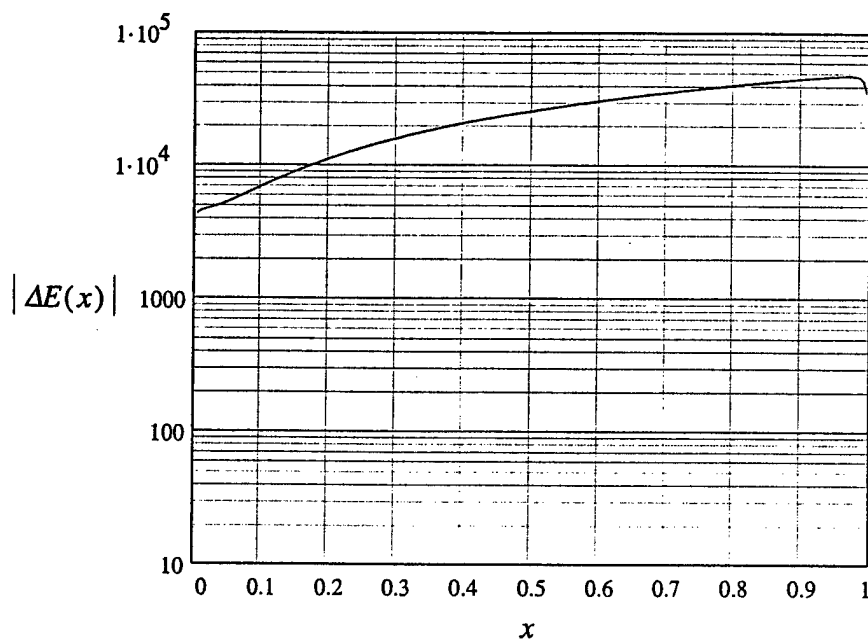
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Figure 10: Developed space charge field (V/cm) versus oxidation state of a saturated hologram recorded in the crystal described in Figure 2 using the simultaneous fixing technique with m=1.

With the simultaneous fixing method, not only is the resulting hologram stronger but also ΔE is nearly independent of the oxidation state of the crystal, at least for $x > 0.8$, where undesirable dark conductivity that is due to small polarons is minimal. In this region ΔE varies by <20%, so little hologram strength is sacrificed when dehydrated crystals are used. For $x = 0.85$, $\Delta E = 45$ kV/cm, which corresponds to a fixed refractive index change of $8.2 \cdot 10^{-4}$, assuming $r = 30$ pm/V. Moreover, from Figure 3, $M = 40$, so the effective lifetime of the hologram at room temperature is 80 years, given that $\omega_i^{-1} = 2$ years. Thus, in this manner it is indeed possible to record a thermally fixed hologram in Fe-doped LiNbO$_3$ with a large refractive index change and a long lifetime.

Experiments appear to support this conclusion. Figure 11 shows the temporal evolution of a hologram recorded at high temperature in a dehydrated LiNbO$_3$ crystal capable of yielding a large fixed photorefractive index change and displaying the 1.4 eV ionic activation energy. After 5 minutes the writing beams were turned off. Because of

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ionic relaxation the hologram quickly decayed with a time constant of ~1 minute. After development and during continuous illumination at 130 °C, the thermal decay of the hologram was substantially slowed down and a time constant of ~50 minutes was measured. Thus, $M \approx 50$ for this crystal and the projected hologram lifetime at 25 °C is estimated to be ~110 years.
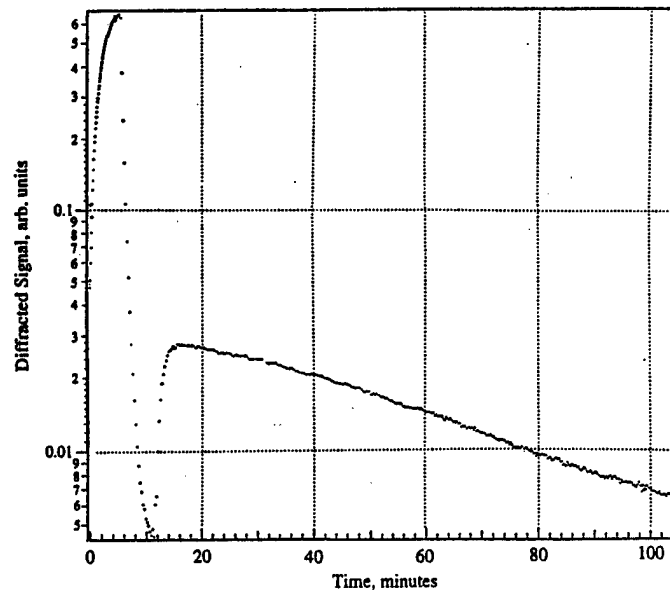

Figure 11:   Temporal evolution of a hologram at 130°C in a dehydrated $LiNbO_3$ crystal displayiong the 1.4eV ionic activation energy.

The key to overcoming the previously unavoidable trade-off between fixed hologram strength and lifetime can be found by examination of Figures 2 and 9. With proper choice of material parameters and the use of the simultaneous fixing technique, ΔN_i acquires a nearly inverse dependence on oxidation state as γ. Therefore, ΔE, which depends on the product of ΔN_i and γ, is only weakly dependent on x, so the oxidation state of the crystal can be freely chosen to increase lifetime without sacrificing much hologram strength.

Extrapolated hologram lifetime estimates that are based on the 1.4 eV activation energy data must be verified by long-term holographic decay measurements near room temperature, since other electrically conducting species with lower activation energies, including residual protons, may ultimately determine the actual decay times at lower temperatures. This can be understood from the curves in Figure 12, which show the ionic relaxation time of a photorefractive hologram in the presence of 2 fixing ions - ordinary 1.2 eV protons and the new 1.4 eV species. At high temperatures the ionic conductivity is primarily due to the 1.4 eV ions, while at lower temperatures protonic conductivity is
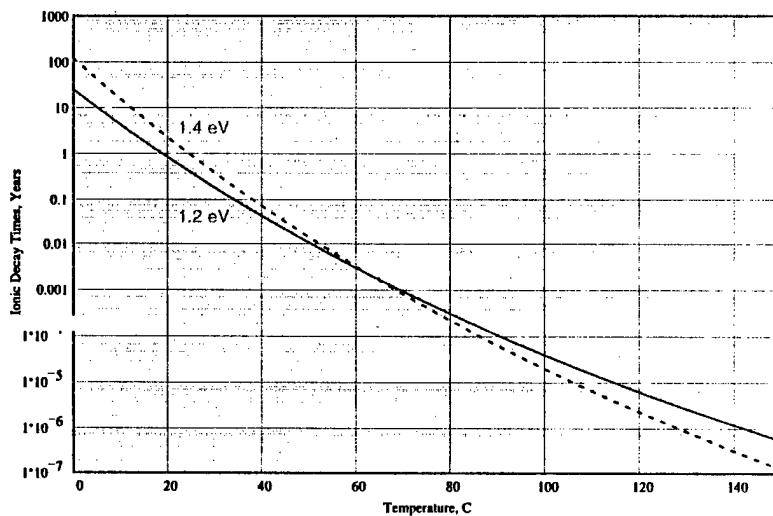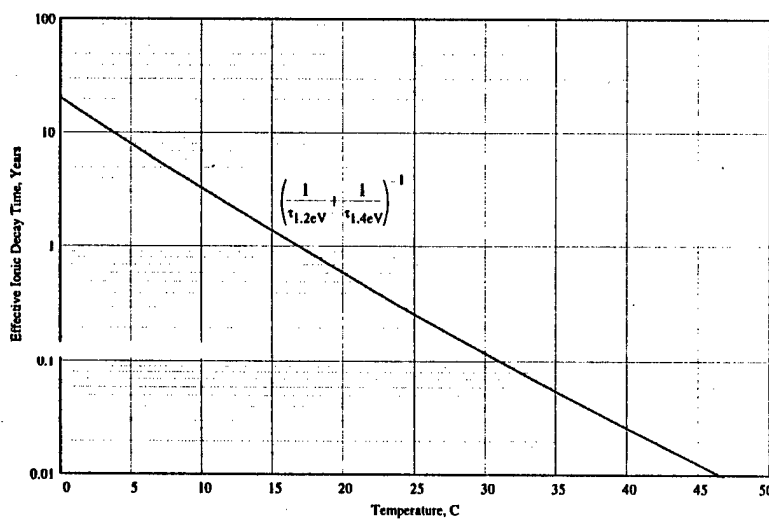
Figure 12a: Decay Times for Individual Ions

Figure 12b: Combined Ionic Decay Time

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dominant. The actual demarcation between these two regions depends on the relative concentration of the two conducting species. In the (hypothetical) example of Figure 12, we see that this transition temperature occurs at 60 °C and that the actual ionic relaxation time ω_i^{-1} at room temperature is much shorter (< 1 year) than the value projected from the 1.4 eV curve. In order to realize the longer 1.4 eV based lifetime in this case, the concentration of protons must be reduced further so that the transition to protonic conductivity occurs at a lower temperature. This additional reduction should be possible by improving the efficacy of the high temperature dehydration process.

In conclusion, thermally fixed holograms in Fe-doped $LiNbO_3$ with high diffraction efficiency and long lifetime can be obtained by the following procedure:

1) Start with a heavily iron-doped $LiNbO_3$ crystal;

2) Increase its ionic relaxation time ω_i^{-1} by dehydration, for example;

3) Anneal the sample to an oxidation state x corresponding to a large lifetime multiplier M without creating an excessive number of small polarons;

4) Electrically short-circuit the c-axis of the crystal;

5) Use the simultaneous fixing method to record the hologram.

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